

Novel Characterization Methods for Microcrystalline Silicon

Final Report
May 1999—December 2002

S.L. Dexheimer and K.G. Lynn
Washington State University
Pullman, Washington



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

Novel Characterization Methods for Microcrystalline Silicon

Final Report
May 1999—December 2002

S.L. Dexheimer and K.G. Lynn
Washington State University
Pullman, Washington

NREL Technical Monitor: R. Matson

Prepared under Subcontract No. AAD-9-18668-01



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

This publication was reproduced from the best available copy
Submitted by the subcontractor and received no editorial review at NREL

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Table of Contents

I.	Overview	1
II.	Materials Studied	2
III.	Methods.....	3
	A. Time-Resolved Optical Techniques	3
	B. Positron Beam Techniques	4
IV.	Highlights of Results.....	5
	A. Carrier Dynamics in Microcrystalline Silicon	5
	B. Carrier Dynamics in a-Si:H and a-SiGe:H	7
	C. Time-Resolved THz Studies of Carrier Trapping	9
	D. Positron Annihilation Spectroscopy of Defects	10
V.	Publication List	12
	Time-Resolved Optical Studies	12
	Positron Annihilation Spectroscopy Studies.....	13

I. Overview

Thin-film microcrystalline silicon and related materials are a promising class of materials currently under development for photovoltaic applications. These materials have attracted considerable interest owing to their high stability, carrier mobility, and doping efficiency, making them promising candidates for low-cost, efficient, and reliable solar cells. The work carried out under this subcontract has provided advanced characterization in support of the development of these materials for photovoltaic applications. The studies, using time-resolved optical methods and positron annihilation spectroscopy, focus on characterization of carrier processes and defect states that are important to understand, and thereby control, to optimize photovoltaic efficiency. This work advances the objectives of the NREL/DOE National Photovoltaic Program by providing unique and innovative characterization methods for photovoltaic materials, by advancing the development of a promising new class of photovoltaic materials through interaction with ongoing materials research at NREL, and by advancing the fundamental scientific understanding of this important class of electronic materials.

In this work, systematic studies as a function of key material parameters have been carried out to develop a more detailed understanding of conductivity processes. Femtosecond laser spectroscopic techniques are used to probe photoexcited carrier processes, including carrier trapping and recombination, as well as carrier thermalization, providing key parameters for conductivity models. An important part of the work involves the application of recently developed methods for generation and detection of femtosecond pulses in the far-infrared (or THz) spectral range. Time-resolved measurements of photoexcited carrier dynamics using far-infrared probe pulses provide a direct measure of the photoconductivity on fast time scales. As discussed below, our time-resolved THz measurements are particularly sensitive to carrier dynamics involving band tail states, and have provided new insight into conductivity processes in disordered electronic materials. Positron annihilation spectroscopy (PAS) measurements on a variety of materials have provided unique information on the nature and concentration of defect states.

II. Materials Studied

The structure of thin-film microcrystalline silicon ($\mu\text{c-Si:H}$, also sometimes referred to as nanocrystalline silicon, or nc-Si:H) can be described qualitatively as a collection of nanometer- to micron-scale silicon crystallites embedded in a hydrogenated amorphous silicon (a-Si:H) matrix. Important material parameters for $\mu\text{c-Si:H}$ include the size of the crystallites and the crystalline fraction, or ratio of the volumes of the crystalline and amorphous components. The composition of the films can be controlled by varying the hydrogen dilution ratio during deposition, yielding materials that span the transition from the amorphous to the microcrystalline state, with increasingly larger grain size and crystalline fraction at higher dilution ratios. “Edge” material at the amorphous to microcrystalline phase boundary has attracted particular interest as a result of its favorable electronic properties and resistance to the photoinduced degradation processes characteristic of thin-film amorphous silicon.

Important issues for the development of this material for photovoltaic applications include understanding the nature of the conductivity mechanism, and especially the role of defects and trapping at the grain boundary regions. An important question addressed by this work is the extent to which the physics of this heterogeneous material can be understood simply as a combination of the properties of the separate phases. We have carried out systematic studies on $\mu\text{c-Si:H}$ in which the material composition is varied through the amorphous to microcrystalline phase transition, and in which the crystallite size and crystalline fraction are systematically varied. To further address issues related to contributions from component phases, we have also carried out studies of a-Si:H and related a-SiGe:H alloys and of bulk crystalline silicon.

Specific materials studied include:

- HWCVD and PECVD $\mu\text{c-Si:H}$ over a range of compositions spanning the amorphous to microcrystalline phase transition (NREL)
- solid-phase epitaxial Si regrown from ion-beam amorphized Si (Caltech)
- PECVD a-Si:H and $\mu\text{c-Si:H}$ (United Solar Systems Corp.)

- HWCVD and PECVD a-Si:H (NREL)
- HWCVD a-Si_xGe_{1-x}:H over a range of compositions $x = 0.02$ to 0.5 (NREL)
- c-Si
- Studies of defects in GaInNAs (NREL) by PAS were also carried out under this subcontract

III. Methods

A. Time-Resolved Optical Techniques

Time-resolved optical measurements were carried out under the direction of Prof. Susan Dexheimer. The femtosecond time-resolved studies are done using the pump-probe technique, in which an ultrashort pump pulse (~ 35 fs in duration) excites carriers in the sample, and a time-delayed probe pulse measures the resulting change in optical properties as a function of delay time between the pump and probe pulses. Wavelength-resolved measurements with wide bandwidth probe pulses allow detection of the transient absorption spectrum, which directly shows the changes in the optical absorption spectrum associated with the evolution of the photoexcited carriers. Detailed measurements of the time-dependent response are made at selected probe wavelengths to measure the dynamics at specific energies. For most of the pump-probe experiments reported below, carriers are excited at transition energies of 1.55 eV or 3.1 eV. The evolution of the photoexcited carrier distribution is measured on femtosecond and picosecond time scales over a range of transition energies, including both above-gap and sub-gap energies. Full technical details on the measurements and instrumentation are given in the publications, as noted below.

An important component of our work involves studies of the dynamics and transport properties of photoexcited carriers made possible by recently developed methods for the generation and detection of femtosecond pulses in the far-infrared (terahertz) spectral range. (For reference, a frequency of 1 THz corresponds to a wavelength of $300\text{ }\mu\text{m}$, and an energy of 4.1 meV or 33 cm^{-1} .) These studies were carried using an optical pump / THz probe technique,

in which carriers are generated with a femtosecond optical pump pulse, and the resulting dynamics are probed using an ultrashort THz pulse that is generated synchronously with the pump pulse. The transmitted THz probe pulse can be spectrally resolved via Fourier analysis of its measured waveform. As a result, the far-infrared spectrum associated with the photoexcitations can be determined as a function of time following the initial excitation. Since the full time-dependent electric field waveform of the transmitted THz pulse can be measured, both the real (index) and imaginary (absorption) part of the far-infrared optical response can be obtained.

Time-resolved spectroscopy using femtosecond THz pulses is an important emerging technique. Time-domain THz spectroscopy directly probes the conductivity mechanisms in electronic materials, since the frequency dependent complex conductivity associated with the carriers is directly proportional to the measured far-infrared response. The THz frequency range corresponds to typical inverse scattering times in electronic materials, making this an important frequency range to study for comparison of the measured frequency-dependent conductivity with physical models. As shown in our work below, THz measurements provide unique insight into transport in disordered systems, since the THz spectral range spans the energy distribution of band tail states that dominate carrier transport in these materials. The apparatus used for our time-resolved THz measurements is discussed in detail in publication [10].

B. Positron Beam Techniques

Positron annihilation spectroscopy (PAS) studies were carried out under the direction of Prof. Kelvin Lynn. The PAS techniques, which directly probe the electron momentum distribution in the material, have been used to characterize the nature and concentration of defect states. All variants of PAS are based on the fact that, upon annihilation with an electron, the combined momentum of the electron-positron pair will cause small deviations (Doppler shifts) in the energies of the two emerging photons, as well as deviations in angle from the center of mass frame. Since the positron predominantly thermalizes before annihilation, its momentum contribution can be neglected relative to that of the electron in almost all cases.

Doppler broadening (DB) PAS spectroscopies integrate over a significant fraction of the angular distribution, but preserve the momentum shifts parallel to the sample detector axis (Doppler shifts). In this technique, the annihilation line is energy-resolved and its shape is parametrized into two values traditionally called S and W. While the S (or line Shape) parameter is mostly sensitive to changes in low Doppler shift annihilations stemming from open volume defects, the W (or Wing) parameter is more sensitive to variations in the contributions from annihilations involving core electrons, which are more tightly bound and thus generally give rise to larger Doppler shifts. Positron lifetime measurements provide complementary information on defect type and concentration. Additional details of PAS measurement techniques are discussed in publication [16].

IV. Highlights of Results

A. Carrier Dynamics in Microcrystalline Silicon

In this work, which is reported in publications [3-7], we carried out high sensitivity and high time-resolution measurements on a series of $\mu\text{c-Si:H}$ and edge materials of systematically controlled composition. This work provided the first definitive interpretation of photoexcited carrier dynamics in $\mu\text{c-Si:H}$, and in particular, demonstrated that the fast carrier processes can be understood in terms of distinct contributions from each component phase of the heterogeneous material.

The microcrystalline silicon thin films studied in these experiments were grown by Dr. Qi Wang at NREL. The thin films were grown on glass substrates by the hot-wire assisted chemical vapor deposition (HWCVD) technique, and the composition of the materials was controlled by variation of the hydrogen dilution ratio $R = \text{H}_2/\text{SiH}_4$ during deposition. The films were deposited at a substrate temperature of 240 °C, and the hydrogen dilution ratio was varied between 1 and 20 with a constant gas pressure of 30 mTorr. Prior to our time-resolved optical measurements, these samples had been extensively characterized by x-ray diffraction, Raman spectroscopy, optical absorption, and photoluminescence. X-ray diffraction measurements indicate that the threshold for the structural transition from amorphous to microcrystalline growth occurs at a

hydrogen dilution ratio $R = 3$, and give an average crystallite size of greater than ~ 10 nm. The x-ray measurements, together with Raman measurements, indicate that both the grain size and crystalline fraction increase with hydrogen dilution above the amorphous to microcrystalline transition. (These measured parameters are reported along with the time-resolved data in publication [5].)

Details of the femtosecond pump-probe measurements are provided in publications [4] and [5]. Briefly, carriers are excited by a pump pulse 35 fs in duration centered at 800 nm (1.55 eV), and the resulting change in transmittance due to the photoexcited carrier distribution is probed over a range of wavelengths in the near-infrared using a compressed femtosecond white-light continuum. Measurements were made over a range of initial carrier excitation densities of $\sim 10^{18}$ to 10^{19} cm $^{-3}$. In all samples, photoexcitation of carriers resulted in a net induced absorbance signal. In the small signal limit, the differential transmittance measurements are expected to be proportional to the photoinduced carrier population, and the time course of the signal reflects the dynamics of the photoexcited carrier distribution.

Analysis of the time-resolved measurements on the microcrystalline materials (discussed in more detail in publications [4] and [7]) revealed three components in the response, corresponding to a carrier population that undergoes a simple exponential decay with time constant $\tau = 240$ fs, a carrier population that undergoes bimolecular recombination, and a long-lived component that decays slowly compared to the ~ 40 ps total time scale of the measurements. The fast, 240 fs exponential response is a new observation in $\mu\text{c-Si:H}$, which we identified as carrier thermalization within the silicon crystallites. This assignment was confirmed by time resolved measurements on c-Si wafers, which were thinned to allow direct transmission measurements, and is also consistent with correlation of the magnitude of the component with the crystalline fraction of the material over the series of samples of systematically varied composition. The detection of this component establishes the carrier-lattice thermalization time within the crystalline phase of the material, in which carriers initially excited above the band gap relax toward the band edge via LO phonon emission, and indicates that the initial carrier relaxation dynamics within the silicon crystallites are representative of those of bulk crystalline silicon. We note that the crystallites in these HWCVD materials are

larger than the expected quantum confinement size of $\sim 4 - 5$ nm for silicon, providing motivation for future work on nanocrystalline silicon materials in the quantum confined limit, in which the carrier cooling dynamics may be significantly altered. Following the initial fast carrier thermalization, the dynamics in HWCVD $\mu\text{c-Si:H}$ are dominated by an excitation density dependent bimolecular recombination component consistent with that seen in a-Si:H , indicating that this part of the response originates from the amorphous fraction of the material. Based on correlation of its amplitude with estimates of the grain boundary fraction, the observed slowly varying third component may include contributions from long-lived carrier states associated with the grain boundary regions.

The materials at and below the amorphous to microcrystalline transition show markedly different dynamics from the microcrystalline materials, especially at short times. The edge material and materials deposited at hydrogen dilution ratios below the amorphous to microcrystalline transition show a time-resolved response characteristic of the relaxation processes we previously observed in a-Si:H , motivating further systematic studies of this material, as discussed in section IV.B below. In particular, on a subpicosecond time scale, the response shows the rapid rise dynamics that we discovered in our initial high-time resolution measurements on a-Si:H and a-SiGe:H , as first reported in publication [1]. For pump-probe delay times greater than ~ 1 ps, the time-dependent optical response can be well characterized by bimolecular recombination, together with a small constant offset, consistent with the response measured in a large body of earlier work on a-Si:H . Comparison of the results for edge materials with a-Si:H indicates that, remarkably, even though edge material shows evidence of some degree of microcrystallinity in the x-ray diffraction and Raman measurements, the optical response of the photoexcited carriers is largely characteristic of a-Si:H , suggesting that, on a microscopic level, the relevant carrier processes for the photoexcitations may be those associated with the amorphous phase of the material.

B. Carrier Dynamics in a-Si:H and a-SiGe:H

As noted above, studies of carrier dynamics in a-Si:H are important for developing a more detailed understanding of the carrier processes in the heterogeneous $\mu\text{c-Si:H}$ and edge

materials. Our studies are also of direct interest, since they address a number of important issues involving fundamental carrier processes in a-Si:H that had remained unresolved, despite a large body of previous time-resolved optical work in this material. One important unresolved issue in the dynamics of photoexcitations in amorphous silicon has been the determination of the time scale for the initial carrier thermalization processes. The carrier thermalization rate is a key parameter for understanding the transport properties of the material, and also provides important insight into the role of disorder in the physics of the carrier processes. In this work, we carried out carefully designed high time resolution measurements that reveal the carrier thermalization dynamics, in which carriers that are initially photoexcited into extended states in the conduction and valence bands relax in energy toward the band edge via phonon emission. In addition, we detect spectral signatures associated with the subsequent lattice equilibration, providing evidence for significantly enhanced phonon redistribution rates in the amorphous material relative to those characteristic of crystalline material. Detailed accounts of the optical pump-probe studies on a-Si:H are presented in publications [8] and [12]. The time-resolved THz measurements discussed in section IV.C below provide complementary insight into carrier localization dynamics in these materials.

Thin films samples for these studies were grown on glass substrates by the hot-wire chemical vapor deposition (HWCVD) technique by Dr. Brent Nelson at NREL. Time-resolved differential transmittance measurements were carried out using the pump-probe technique, in which carriers are excited well above the band gap via two-photon absorption of a 35 fs pump pulse centered at 800 nm, and the resulting change in transmittance due to the photoexcited carrier distribution is probed at both sub-gap and above-gap transition energies using a compressed femtosecond white-light continuum. Accompanying time-resolved optical measurements on a-Si_xGe_{1-x}:H as a function of composition were also carried out as a part of these studies.

The time-resolved measurements were interpreted using a multi-component analysis. Rapid, subpicosecond relaxation components and their associated spectroscopic signatures were detected in our high time resolution measurements, in addition to the population dynamics on picosecond and longer time scales corresponding to previously documented bimolecular

recombination. Thermalization of carriers toward the band edge states via phonon emission results in an increase in the population of states of lower energy with time, and this effect is detected in our measurements by the associated bleaching of optical transitions involving the newly filled states. It is interesting to note that our observed time scale of ~ 150 fs for the carrier cooling in a-Si:H is comparable, though somewhat faster than the ~ 240 fs time scale that we detected for the analogous process in crystalline silicon. Further equilibration of the lattice is detected in our measurements via its effect on the temperature-dependent optical absorbance, and we find evidence for energy redistribution among the phonon modes in a-Si:H on a time scale of ~ 230 fs. Interestingly, this process takes place on a significantly more rapid time scale in amorphous silicon than in crystalline semiconductors, likely as a result of increased coupling between phonon modes.

C. Time-Resolved THz Studies of Carrier Trapping

In this work, which is reported in publications [10] and [12], we carried out femtosecond time-resolved studies of the photoexcited carrier response in the far-infrared spectral range in PECVD a-Si:H and a-SiGe:H thin films. These experiments are carried out using the optical pump / terahertz (THz) probe technique described in section III above, in which a femtosecond pump pulse excites carriers in the sample and a time-delayed probe pulse measures the resulting change in the far-infrared optical properties as a function of time delay following the excitation. These measurements are sensitive to carrier processes at low energy, corresponding to a range of approximately 1 - 10 meV, a key energy scale in these materials.

Our time-resolved THz studies on provide new insight into conductivity processes in disordered systems. A large body of previous time-resolved measurements on a-Si:H and related materials on picosecond and femtosecond time scales carried out at visible and near-infrared probe wavelengths showed a response dominated by carrier population loss with kinetics consistent with bimolecular recombination, but the detailed nature of the carrier processes had remained unclear. Our measurements in the THz frequency range reveal a dramatically different response, allowing us to detect a new component of the carrier dynamics that reflects the time-dependent mobility of the photoexcited carrier distribution as carriers initially excited into

extended states trap into the exponential distribution of band tail states that dominate the conductivity processes in these materials. These experiments establish the time scale and dynamics of this fundamental carrier localization process.

Optical pump / THz probe measurements were carried out over a range of initial excitation densities. As shown in publication [10], the measurements are quantitatively modeled in terms of a time-dependent conductivity that includes both the time-dependent mobility and the population loss due to bimolecular recombination. We find that carrier trapping, which occurs over a distribution of time scales, is largely complete within picoseconds in the amorphous thin film materials, and the time course of the dynamics is specific to the detailed material properties. Frequency-resolved measurements of the far-infrared response of the photoexcited carrier distribution show a strongly non-Drude behavior reflecting the influence of the disorder on the conductivity.

D. Positron Annihilation Spectroscopy of Defects

Depth dependent positron annihilation spectroscopy was used to study open volume type defects in amorphous and microcrystalline Si thin films prepared at United Solar Systems Corp. This work was reported in publication [16]. The films were deposited by plasma enhanced chemical vapor deposition (PECVD) onto steel substrates. The data indicate that the amount of hydrogen dilution during the growth process determines the amount of open volume seen by positrons. Higher dilution ratios result in material properties more like those for single crystal silicon and are known to promote micro-crystalline growth. The efficiency of a-Si:H solar cells initially degrades under illumination, but can be recovered by annealing at about 200 C. In positron annihilation measurements the illumination-induced change is observed, but no clear indication of the reversal has been found. A second irreversible defect in addition to the reversible Staebler-Wronski defect must be present. The effects of illumination are smaller in samples grown in H-dilution conditions. Further studies on a systematic series of samples in a form that is compatible with multiple characterization techniques would be promising for developing a more detailed understanding of the light-soaking effects.

PAS was used to study defects in solid-phase epitaxial Si regrown from ion-beam amorphized layers (materials from Caltech) in work reported in publications [13] and [14]. Silicon single crystal wafers were implanted with boron, phosphorous and both P and B ions after pre-amorphization with ^{29}Si ions. Recrystallization was then performed to several depths by annealing at 600 C for different times (solid phase epitaxy SPE). The regrowth process was monitored by in situ time resolved reflectivity (TRR) measurements. The samples were examined by positron annihilation spectroscopy (PAS) to observe open volume type defects. To increase the depth resolution of the technique, thin 34 nm layers were etched off alternating with positron measurements. The recrystallization of the amorphized layer could clearly be observed. Defects in the end of range region could not be removed in the annealing steps. The regrowth process is different depending on the species of implanted ion. P implantation appears to result in recrystallizations closest to pre implantation conditions. It was observed that oxygen atoms are transferred into the implantation region from primary ion recoils. During the annealing O-vacancy complexes are formed.

Finally, PAS measurements were also carried under this subcontract on GaInNAs materials from NREL. This work is reported in publications [18] and [19]. Motivated by recent theoretical calculations involving the effect of hydrogen on the formation energy for gallium vacancies, we carried out a comparison of defects in materials grown by MOCVD and by solid-source MBE, with and without an atomic hydrogen flux. Of the MBE-grown samples, only the material grown under hydrogen flux shows a significant V_{Ga} signal, indicating that hydrogen facilitates the vacancy formation. Results indicate a higher V_{Ga} concentration for the MOCVD GaInNAs material, and show that annealing reduces, but does not eliminate the defects. In a separate study, positron annihilation measurements were carried out on boron-implanted GaInNAs, with results suggestive of at least two types of vacancy related defects, providing motivation for future studies.

V. Publication list

Time-Resolved Optical Studies

1. Ultrafast dynamics of photoexcitations in HWCVD hydrogenated amorphous silicon alloys. J.E. Young, B.P. Nelson, and S.L. Dexheimer, *Materials Research Society Symposium Proceedings* vol. 609: Amorphous and Heterogeneous Silicon Thin Films, A20.1 (2000).
2. Ultrafast dynamics of photoexcited carriers in HWCVD a-Si:H and a-SiGe:H. S.L. Dexheimer, J.E. Young, and B.P. Nelson, Program and Proceedings: NCPV Program Review Meeting 2000, 16-19 April 2000, Denver, CO, BK-520-28064, p. 227-228 (2000).
3. Femtosecond carrier dynamics in nanocrystalline silicon films: The effect of the degree of crystallinity. Myers, K.E., Wang, Q., and Dexheimer, S.L., *Materials Research Society Proceedings* v. 664 A16.5 (2001).
4. Ultrafast carrier dynamics in nanocrystalline silicon. Myers, K.E., Wang, Q., and Dexheimer, S.L. *Phys. Rev. B* **64** Rapid Communications 161309(R) (2001).
5. Ultrafast carrier dynamics through the transition from amorphous to microcrystalline silicon. Dexheimer, S.L., Myers, K.E., Young, J.E., Nelson, B.P., and Wang, Q., in *Photovoltaics for the 21st Century II*, Electrochemical Society Proceedings, vol. 2001-10, R.D. McConnell and V.K. Kapur, eds. (2001).
6. Phase-dependent carrier processes in silicon-based photovoltaic materials, Dexheimer, S. L., Myers, K. E., Liu, J., Wang, Q., and Nelson, B. P., National Center for Photovoltaics Review Proceedings (2001).
7. Ultrafast carrier dynamics in thin-film nanocrystalline silicon. Dexheimer, S.L., Myers, K.E., and Wang, Q., in *Ultrafast Phenomena in Semiconductors VI, SPIE Proc.*, v. **4643**, 62 (2002). Invited paper.
8. Ultrafast carrier thermalization in hydrogenated amorphous silicon. Dexheimer, S.L., Zhang, C.P., Liu, J., Young, J.E., and Nelson, B.P., *Materials Research Society Proc.* v. **715**, A2.1 (2002).
9. Phase-dependent ultrafast carrier and lattice relaxation: Amorphous, crystalline, and nanocrystalline silicon. Dexheimer, S.L., Zhang, C.P., Liu, J., Myers, K.E., Young, J.E., Wang, Q., and Nelson, B.P., in *Ultrafast Phenomena XIII*, Springer Series in Chemical Physics v. **71**, 380, R.J.D. Miller, M.M. Murnane, N.F. Scherer, and A.M. Weiner, eds. (2002).
10. Femtosecond far-infrared studies of carrier dynamics in hydrogenated amorphous silicon and silicon-germanium alloys. Nampoothiri, A.V.V., Nelson, B.P., and Dexheimer, S.L., Materials Research Society, in press (2003).

11. Initial stages of carrier trapping in hydrogenated amorphous silicon. Nampoothiri, A.V.V., Nelson, B.P., and Dexheimer, S.L. (manuscript in preparation)
12. Ultrafast thermalization dynamics in hydrogenated amorphous silicon. Zhang, C.P., Liu, J.H., Young, J.E. Nelson, B.P. and Dexheimer, S.L. (manuscript in preparation)

Positron Annihilation Spectroscopy Studies

13. Study of Vacancy and Impurity Complexes in Si Solid-Phase Epitaxial Crystallization with Positron Annihilation Spectroscopy. C.M. Chen, S. Rassiga, M. Petkov, M.H. Weber, K.G. Lynn, H.A. Atwater, MRS Symposium Proceedings, Vol. 609: Amorphous and Heterogeneous Silicon Thin Films (2000).
14. A Relation Between Surface Oxide and Oxygen-Defect Complexes in Solid-Phase Epitaxial Si Regrown from Ion-Beam-Amorphized Si Layers. M.P. Petkov, C.M. Chen, H.A. Atwater, S. Rassiga and K.G. Lynn, Appl. Phys. Lett. Vol. 76, 1410 (2000).
15. Defect profiling of thin-film microcrystalline silicon using positron annihilation spectroscopy. S. Rassiga, K.G. Lynn, H. Mahan, B.P. Nelson, NCPV Program Review Meeting 2000, 16-19 April 2000, Denver, CO.
16. Positron annihilation studies on a-Si thin films, M.H. Weber, T. Gessmann, K.G. Lynn, R.S. Crandall, J. Yang, and S. Guha, in *Photovoltaics for the 21st Century II*, Electrochemical Society Proceedings, vol. 2001-10, R.D. McConnell and V.K. Kapur, eds. (2001).
17. Positron investigations of thin film silicon for photovoltaics, K.G. Lynn, M.H. Weber, C.-L. Wang, S.P. McNeil, NCPV Program Review Proceedings (2001).
18. Defects in GaInNAs: What We've Learned So Far. A.J. Ptak, S. Kurtz, S.W. Johnston, D.J. Friedman, J.F. Geisz, J.M. Olson, W.E. McMahon, A.E. Kibbler, C. Kramer, M. Young, S.-H. Wei, S.B. Zhang, A. Janotti, P. Carrier, R.S. Crandall, B.M. Keyes, P. Dippo, A.G. Norman, W.K. Metzger, R.K. Ahrenkiel, R.C. Reedy, L. Gedvilas, B. To, M.H. Weber, and K.G. Lynn, National Center for Photovoltaics and Solar Program Review Meeting, March 2003.
19. Positron Annihilation Study of vacancies in GaInNAs. A.J. Ptak, Sarah Kurtz, M.H. Weber and K.G. Lynn, North American MBE Conference (NAMBE) Proceedings, 28 Sep 2003 - 02 Oct 2003, Keystone, CO (in preparation).

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 2003	3. REPORT TYPE AND DATES COVERED Subcontract Report May 1999–December 2002		
4. TITLE AND SUBTITLE Novel Characterization Methods for Microcrystalline Silicon: Final Report, May 1999–December 2002		5. FUNDING NUMBERS PVP42100 AAD-9-18668-01		
6. AUTHOR(S) S.L. Dexheimer and K.G. Lynn				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Washington State University Pullman, Washington 99164-2814		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-520-34949		
11. SUPPLEMENTARY NOTES NREL Technical Monitor: Richard Matson				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
<p>13. ABSTRACT (Maximum 200 words): The work carried out under this subcontract has provided advanced characterization supporting the development of these materials for photovoltaic applications. The studies, using time-resolved optical methods and positron annihilation spectroscopy, focus on characterization of carrier processes and defect states that are important to understand, and thereby control, to optimize photovoltaic efficiency. This work advances the objectives of the NREL/DOE National Photovoltaic Program by providing unique and innovative characterization methods for photovoltaic materials, by advancing the development of a promising new class of photovoltaic materials through interaction with ongoing materials research at NREL, and by advancing the fundamental scientific understanding of this important class of electronic materials.</p> <p>In this work, systematic studies as a function of key material parameters have been carried out to develop a more detailed understanding of conductivity processes. Femtosecond laser spectroscopic techniques are used to probe photoexcited carrier processes, including carrier trapping and recombination, as well as carrier thermalization, providing key parameters for conductivity models. An important part of the work involves the application of recently developed methods for generation and detection of femtosecond pulses in the far-infrared (or THz) spectral range. Time-resolved measurements of photoexcited carrier dynamics using far-infrared probe pulses provide a direct measure of the photoconductivity on fast time scales. As discussed below, our time-resolved THz measurements are particularly sensitive to carrier dynamics involving band tail states, and have provided new insight into conductivity processes in disordered electronic materials. Positron annihilation spectroscopy (PAS) measurements on a variety of materials have provided unique information on the nature and concentration of defect states.</p>				
14. SUBJECT TERMS: PV; microcrystalline silicon; thin-film; positron annihilation spectroscopy; femtosecond laser spectroscopic; X-ray diffraction; photoluminescence; hot-wire chemical vapor deposition; `			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	